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For additional copies and more information, please write to the editors ;

Professor T. Ishikawa, Electrometallurgy Laboratory,
Professor M. Seo, Electrochemistry Laboratory,
Professor H. Ohashi, Nuclear Reactor Materials Laboratory,
Professor R. Furuichi, Analytical Chemistry Laboratory,
Professor T. Narita, Composite Materials Processing and Evaluation Laboratory.

Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8,
Kita-ku, Sapporo 060, Japan

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ELECTROCHEMISTRY LABORATORY

Prof. Dr. M. Seo, Assoc. Prof. Dr. H. Takahashi,
Dr. K. Azumi, Dr. K. Noda and Miss. J. Fujiwara

Students

K. Fujiwara, K. Yoshida, K. Shigyou, K. Nukui, M. Koike,
M. Shikanai, Y. Hirota and Y. Yamamoto

The research activity of the laboratory still continues to be directed towards a better undersanding of the interfacial properties of metal and semiconductor electrodes in relation to the interfacial electrochemistry involving corrosion, passivation, anodic oxidation, surface finishing, and surface coating.

(1) Piezoelectric response to underpotential deposition of Ag on Au electrode

The underpotential deposition (UPD) of Ag on Au electrode in perchlorate and sulphate solutions has been investigated from the piezoelectric response of surface stress change induced by a potential modulation. Two characteristic potentials at which the amplitude of piezoelectric signals, $|A|$, took minimum and the phase angle of piezoelectric signals, ϕ, changed by 140° appeared during UPD of silver. The lower one, E_1, and higher one, E_2, of characteristic potentials correspond to electrocapillary minimum and maximum, respectively. The appearance of E_1 and E_2 will be explained in terms of coadsorption of electrolyte anions with silver adatoms. The potential E_1 in sulfate solution is higher than that in perchlorate solution, whereas the situation is opposite on E_2. The strong dependence of electrolyte anions on E_1 and E_2 is attributed to the difference in binding strength of electrolyte anions with silver adatoms.

(2) QCM study on corrosion of iron thin films in neutral aqueous solutions

A quartz crystal microbalance (QCM) technique was applied to investigate the corrosion of iron thin films in deaeraed pH 6.48

boric-borate solution, pH 6.42 borate solution with 10^{-2} M chloride ions, pH 6.0 borate solution with 0.5 M chloride ions, and pH 6.48 phosphate solution. The iron thin films with a thickness of 200 nm were electroplated on gold electrode on quartz oscillator in $FeSO_4$ $(NH_4)_2SO_4 \cdot 6H_2O$ solution.

The dissolution rate of iron thin films at natural immersion in these solutions were measured from the time variation of mass loss. The net current flowed through the external circuit during galvanostatic polarization near the corrosion potential was successfully separated into the iron dissolution current and hydrogen evolution current. The Tafel plots of the iron dissolution current and hydrogen evolution current were made to evaluate the corrosion mechanism of iron thin film. The Tafel slopes of iron dissolution and hydrogen evolution depended on the electrolyte solutions from which the corrosion mechanism was discussed.

(3) Measurement of electroluminescence from porous Si during anodic oxidation

Single-crystal p-type Si (100) wafers with a specific resistivity of 10 ohm cm were galvanostatically etched in aqueous and ethanol solutions with different HF concentrations to prepare the porous structures. The electroluminescence (EL) in the wavelength range of visible red light was emitted from the porous layers of Si during anodic oxidation in 0.1 M KNO_3 solution and depended sensitively on the etching conditions. The surface morphology and composition of porous Si are being investigated by SEM, AFM and FT–IR.

(4) Electrochemistry of carbon steel in deaerated carbonate solutions

A carbon steel is regarded as one of candidates of overpack materials for long term storage of nuclear waste in reducing environments of underground. The potentiodynamic polarization curves of carbon steel were measured in deaerated carbonate solution with different pHs and concentrations. The thickness of passive film formed potentiostatically on carbon steel was estimated from the electric charge for cathodic reduction of the film and increased with increasing the potential of film formation. The depth-composition profiles of passive films were measured by using Auger Electron Spectroscopy combined with argon-ion sputteretching technique, revealing that no carbonate is present in the film.

(5) Cathodic polarization of aluminum covered with anodic oxide films

Cathodic polarization behavior of aluminum covered with various types of anodic oxide films has been examined by potential sweep in a neutral borate solution by measuring the current-time curves, the number and size of pits formed during cathodic polarization, and the amount of dissolved Al^{3+} ions. The imperfections in the anodic oxide films were evaluated semi-quantitatively from the cathodic polarization. The anodic oxide films formed after thermal oxidation showed the most defective structure, whereas barrier type oxide films formed on smooth surface had less imperfections.

(6) Anodizing of aluminum with laser irradiation

Aluminum covered with several types of oxide film was anodized in a sulfuric acid solution after the irradiation of a pulse-YAG laser to form porous type anodic oxide films at the laser irradiated area. A pore-branching oxide film was found to grow at the laser-irradiated area at a rate lower than that during conventional anodizing, which does not depend on the type and thickness of preexisting oxide films.

(7) Formation of Ti/Al-composite oxide films on aluminum by the pore-filling method

Aluminum covered with a porous anodic oxide film was immersed in potassium titanium oxalate solutions, and then heated to decompose the salt adsorbed on the pore surface. After heating the specimen was anodized in a neutral borate solution to allow the pore to be filled with Ti/Al composite oxide. The porefilling rate increased with increasing heating temperature and the number of repetition of immersion/heating.

Other Activities

Prof. M. Seo attended the 44th Meeting of International Soc.

of Electrochem. (ISE), which was held in Berlin, Germany, on September 5-10, and presented a paper entitled "Piezoelectric Detection of Underpotential Deposition of Silver on Gold Electrode". Afterward, he visited Professor J. W. Schultze at Institute of Physical Chemistry and Electrochemistry, Heinrich-Heine University, Dusseldorf, Germany, on September 13-14, and Professor W. H. Smyrl at Corrosion Resarch Center, University of Minnesota, Minneapolis, U.S.A. on September 16-17. Furthermore, he attended the 12th International Corrosion Congress (ICC), which was held in Houston, Texas, U.S.A., on September 19-23, and presented a paper entitled "In-Situ Gravimetry of Corrosion of Iron Thin Films Combined with Surface Analytical Techniques"

Dr. H. Takahashi attended the 183rd Electrochem. Soc. Meeting co-sponsored by the Electrochem. Soc. Jpn. at Honolulu, Hawaii on May 16-21, and presented papers entitled "Breakdown of Anodic Oxide Films on Aluminum by Cathodic Polarization in a Neutral Borate Solution" and "Electroluminescence from p-Type Silicon during Anodic Oxidation and Breakdown of the Anodic Oxide Films". Dr. K. Azumi is still spending a sabbatical leave at the Department of Materials Science and Engineering, Stanford University, California.

The following foreign scientists visited this laboratory: Dr. J. S. Cross, visiting researcher at National Institute for Research in Inorganic Materials (U.S.A.) on October 1, Dr. W. Vajragupta, Assistant Professor, Dept. of Metallurgical Engr., C. Hultquist, Associate Professor, Royal Institute of Technology, Sweden on October 29- November 27, Drs. B. Mishima, and H. Mishima, Institute of Ciencias Quinicas, F. A. A. Univ. Nac. de Santiago del Estero, Argentina, on December 7-10.

Presentations

Study of UPD of Silver on Gold Electrode by Piezoelectric Response; M. Aomi, and M. Seo: The 19th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Sapporo, Jan., 1993.

Pursuit of Passivation Process of Electroplated Iron Thin Film; M.

Seo, K. Yoshida and K. Noda: *ibid.*

Pit Formation on Aluminum Covered with Anodic Oxide Films by Cathodic Polarization; K. Fujiwara, H. Takahashi and M. Seo: The 2nd Hokkaido Section Meeting of Jpn. Soc. Corros. Eng., Sapporo, Jan., 1993.

Photo-Electrochemical Behavior of TiN Films Coated on Platinum and Stainless Steel; S. Watanabe, K. Azumi and M. Seo: The 1993 Winter Meeting of The Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., Sapporo, Feb., 1993.

Anodizing of Aluminum with Heat Treatment. —Effect of Anodizing Temperature on the Film Formation—; M. Dairaku, H. Takahashi and M. Seo: *ibid.*

Anodic Oxidation and Film Structure of Valve Metals; M. Seo: The 87th Annual Meeting of Surface Finishing Soc. Jpn., Yokohama, March, 1993.

Effect of Film Structure on The Cathodic Polarization of Aluminum in a Neutral Borate Solution; K. Fujiwara, H. Takahashi and M. Seo: *ibid.*

Study on UPD Process by a Piezoelectric Response; M. Seo and M. Aomi: The 60th Meeting of Electrochem. Soc. Jpn., Tokyo, April, 1993.

Structure and Formation Mechanism of Thermal/Anodic Composite Oxide Films on Aluminum; H. Takahashi, M. Dairaku and M. Seo: *ibid.*

Application of Mechanically Equivalent Circuit of QCM to Corrosion Process of Metal Thin Film; M. Seo and K. Noda: '93 Spring Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1993.

Anodizing of Aluminum Die-Casting Alloys. —Effect of Chemical Composition and Solidification Method Film Formation; H. Takahashi, K. Shiga and M. Seo: *ibid.*

Breakdown of Anodic Oxide Films on Aluminum during Cathodic Polarization in a Neutral Borate Solution; H. Takahashi, K. Fujiwara and M. Seo: the 183rd Meeting of Electrochem. Soc., Honolulu, Hawaii, May, 1993.

Electroluminescence from p-Type Silicon during Anodic Oxidation and Breakdown of the Anodic Oxide Films; M. Seo, K.

Fushimi, H. Takahashi and K. Aotsuka : *ibid.*

Introduction to Anodizing of Aluminum ; H. Takahashi : Seminar on Surface Finishing Sponsored by Surface Finishing Soc. Jpn., Tokyo, June, 1993.

Electroluminescence from Anodic Oxide Films on Niobium and Titanium during Cathodic Polarization ; K. Shigyou, K. Noda, H. Takahashi and M. Seo : The 1993 Summer Meeting of The Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Anal. Chem., Kushiro, July, 1993.

Anodizing of Aluminum under Laser Irradiation ; K. Nukui, H. Takahashi, M. Seo, M. Kawasaki and Y. Matsumi : *ibid.*

Dielectric Properties of Anodic Oxide Films on Aluminum ; H. Takahashi : The 1993 Summer Seminar Co-sponsored by Hokkaido Sections of Surface Finishing Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Aug., 1993.

Piezoelectric Detection of Underpotential Deposition of Silver on Gold Electrode ; M. Seo, M. Aomi and K. Yoshida : The 44th Meeting of International Society of Electrochemistry, Berlin, Germany, Sept., 1993.

In-Situ Gravimetry of Corrosion of Iron Thin Films Combined with Surface Analytical Techniques ; M. Seo and K. Yoshida : The 12th International Corrosion Congress, Houston, Texas, Sept., 1993.

Polarization Behavior and Photo-Electrochemical Characteristics of TiN Film in Borate Solution ; M. Seo, S. Watanabe and K. Azumi : The 88th Annual Meeting of Surface Finishing Soc. Jpn., Nagoya, Oct., 1993.

Local Anodizing of Aluminum with YAG-Laser Irradiation ; K. Nukui, H. Takahashi, M. Seo, M, Kawasaki and Y. Matsumi ; *ibid.*

Recent Investigation of Anodizing of Aluminum and Its Alloys ; H. Takahashi ; Seminar on Surface Finishing Sponsored by Hokkaido Surface Finishing Research Institute, Sapporo, Oct., 1993.

The Effect of Anions on Corrosion Behavior of Electroplated Iron Thin Films ; K. Yoshida, K. Noda and M. Seo : The 40th Symp. on Corrosion and Protection, Naha, Nov., 1993.

Effect of Imperfections of Oxide Films on the Cathodic Polarization Behavior of Aluminum; K. Fujiwara, H. Takahashi and M. Seo: *ibid.*

QCM Analysis of Corrosion Process of Metal Thin Films; M. Seo, K. Noda and K. Yoshida: Seminar on Green Materials, Sendai, Nov., 1993.

NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. H. Ohashi, Assoc. Prof. Dr. S. Sato, Dr. T. Mizuno,
Mr. T. Kozaki, Mr. K. Hirohara and Miss R. Oyama

Students

Y. Torikai, T. Fukuda, M. Samadfam, Y. Imamura, A. Ohashi,
Y. Miyazaki, T. Kuroda, K. Takano, H. Tamai and Y. Niitu

The current research activities of the laboratory are mainly concerned with corrosion of metallic materials used in nuclear industry, development of fuel cell using hydrogen reservoir alloys, estimation of pitting corrosion, migration of noble metal fission products in UO_2, and radioactive waste management.

(1) Hydrogen storage alloys as electrodes of the fuel cell, i.e., La-Ni and Mm-Ni were studied in an aqueous solutions. Several types of alloy system were prepared in various conditions. All alloys were first activated, then pulverized to small particles, mechanically compressed, and sintered. The alloy specimens obtained were examined about stability, i.e., disintegration resistance during charge-discharge cycles in the electrolyte, and it is found that the sintered and activated La-Ni alloy is a promising electrode for the hydrogen storage type fuel cell.

(2) Passivation and pitting of stainleless steel was studied by a spectrum analysis of fluctuation of the corrosion currents. The shape of the spectra was expressed by the relationship of $I=f^n$ $(-1 \leqq n \leqq 0)$ in the range of frequency from 10^{-2} to 10 Hz. The method was applied for, first, estimation of the stability of passive films in the neutral solution and then, prediction of the pit generation.

In the passivation process, spectra changed with increase in the thickness of film, and slope, n, approached to zero. Even after the addition of Cl^- ions, n was nearly zero, while the passive film was stable. However, the change in n appeared, $(-1 \leqq n \leqq 0.5)$, when the film became unstable, and sporadic tiny pits were detected.

(3) Pd is the most corrosive noble metal fission product against SiC in coated particle fuels for high temperature gas-cooled reactors. To clarify the effects of Pd on the fuel performance, the migration behavior of Pd in uranium dioxide pellet has been studied. Penetration profiles of Pd in the pellet were obtained by the electron probe micro-analysis. Diffusion coefficients of Pd were determined at temperatures from 1600 to 2100 K. The diffusion coefficients were in the order of 10^{-15} m^2/s, though the vapor pressure of Pd is 10^{-3} torr at 1700 K. In an attempt to clarify the migration process of Pd, the evaluation of several migration processes was carried out.

(4) The corrosion behavior of overpack materials in bentonite was studied for safety assessment of the geological disposal of the high level radioactive waste. Average corrosion rates of iron and apparent diffusion coefficients of corrosion products were determined, using neutron-activated iron foils and bentonite specimens with different dry densities. The corrosion rates and diffusion coefficients depended on dry density of the bentonite. Quantitative analysis of the corrosion products was also carried out using 1, 10-phenanthrolin as a colorimetric indicator to obtain the concetration profiles of both Fe^{2+} and total Fe and of the Fe^{2+}/total Fe ratio. From the profiles, it is probable that the pH and/or redox potential of the pore water in bentonite would be changed by corrosion of iron. In addition, we studied the behaviour of sodium ion that is the main exchangeable cations of bentonite. The redistribution of sodium ions induced by corrosion was observed in the bentonite-iron system, and apparent self-diffusion coefficients of sodium ions were determined using Na-22 as a radiotracer. The results also suggested the changes of pH and/or redox potential of the pore water in the bentonite.

(5) In connection with the long-term prediction of the migration behavior of radionuclides in compacted bentonite the vapor pressure of water in bentonite (Kunigel-V1) was measured as functions of water content and temperature, under an external pressure free condition. Relative partial molar Gibbs free energy $\Delta G(H_2O)$, enthalpy $\Delta H(H_2O)$ of the water were determined at temperature of 298.15 K. Interlayer distance of montmorillonite in bentonite was also measured and found to be 3 water layers at water content of 20.3 wt % by the X ray diffraction method.

One third of the water in bentonite at the water content is similar to the ordinary water but is not regarded as dilute electrolytic solution. One fourth of the total water of bentonite at the water content is restricted; the relative partial molar entropy of water is from the full entropy of solidification of water to one- half of that. The thermodynamic quantities are considered to be dependent on pore water, interlayer water in montmorillonite and adsorbed water on other minerals as a function of water content.

In addition, to clarify the kinetic properties of water in bentonite, diffusion of tritiated water and argon in compacted bentonite have been studied as functions of temperature and dry density by the liquid scintillation counting and mass spectrometric methods.

(6) For the purpose of safety assessment of land disposal of radioactive waste, the migration behavior of fission products and actinides in geologic formation must be clarified. The study on the migration behavior in the presence of humic acid and fulvic acid is very limited. In this connection, stability constant of Sr with humic acid was determined using Sr-85 as a radiotracer. Sorption coefficients of Sr on pulverized granitic rock and kaolinite were measured by a batch method as functions of contact time, pH, and concentrations of Sr and humic acid.

Presentations

Studies of Pitting Corrosion of Stainless Steel by Spectrum Analysis ;
T. Fukuda, T. Mizuno and H. Ohashi: The Second Annual

Meeting of the Hokkaido Section of the Corrosion Engineering of Japan, Sapporo, Jan. 22, 1993.

Relationships between Deuterium Concentration and Heat Evolution of Palladium ; T. Mizumo : Seminar of the Hokkaido Section of the Electrochemical Society of Japan, Ohtaki, June 12, 1993.

Thermodynamic Properties of Water in Bentonite and Montmorillonite ; Y. Torikai, S. Sato and H. Ohashi : The 1993 Fall Meeting of the Atomic Energy Society of Japan, Kobe, Oct., 1993.

Migration Behavior of Fe Ions in Compacted Bentonite ; Y. Imamura, T. Kozaki, S. Sato, H. Ohashi, J. Takada, T. Ohe, M. Tsukamoto and T. Fujita : The 1993 Fall Meeting of the Atomic Energy Society of Japan, Kobe, Oct., 1993.

Anomalous Heat Evolution from $SrCeO_3$-Type Proton Conductors during Absorption/Desorption of Deuterium in Alternate Electric Field ; T. Mizumo, T. Akimoto, K. Azumi and Enyo : The 4th International Conference on Cold Fusion, Maui, Hawaii, Dec. 6-9, 1993.

Thermodynamic Properties of Water in Compacted Bentonite as Engineered Barrier ; Y. Torikai, S. Sato and H. Ohashi : The 11th Annual Meeting of the Hokkaido Branch of the Atomic Energy Society of Japan, Sapporo, Dec. 16, 1993.

ELECTROMETALLURGY LABORATORY

Prof. Dr. T. Ishikawa, Assoc. Prof. Dr. T. Sasaki,
Dr. T. Notoya and Mr. S. Konda

Students

T. Matsuhashi, M. Nakata, M. Ueda, S. Kobayashi, K. Kondo,
S. Hara, N. Ohya, T. Itoh, H. Shodo and H. Taniguchi

Professor T. Ishikawa attended the 9th International Symposium on Molten Salt in Honolulu, Hawaii, in May, and associate professor T. Sasaki and Dr. T. Notoya attended the 183rd Meeting of Electrochemical Society in the same place.

Dr. T. Notoya was invited to give a couple of lectures on mechanisms of corrosion of copper alloys and its inhibition with organic inhibitors by Professor Guo-ding Zhou at Shanghai Institute of Electric Power in Shanghai, China, on May 29—June 2. Dr. Notoya and Dr. Schweinsberg, Queensland University of Technology in Brisbane, Australia, visited Professor Lu Zhu of East China University of Science and Technology in Shanghai during the time.

Researches in progress are as follows.

(1) Laboratory-scale tests for electrowinning of liquid aluminum and its titanium alloys by using bipolar electrode cells are being carried out in alkali and alkaline earth chloride molten salts containing $AlCl_3$ and/or $TiCl_4$ in the temperature range from 700 to 800°C.

(2) In order to save energy in producing pure aluminum from aluminum scraps, an electrochemical cycle system composed of three stepwise processes in molten salts was developed and the characteristics of one process of the system, the aluminum-chlorine fuel cell, are under study.

(3) Co-deposition reaction of several metals with aluminum in low-

temperature chloride molten salts containing $AlCl_3$ is being studied together with investigation of the characteristics of $AlCl_3$–NaCl containing the chlorides of the metals.

(4) Corrosion characteristics of aluminum layer electrodeposited from room-temperature molten salt baths are being studied in tap water by electrochemical techniques.

(5) The corrosion resistance of various kinds of chromium-containing alloys in sulfuric acids is being evaluated in terms of aging of passive films by electrochemical techniques.

(6) In relation to the corrosion of electronic circuits, electrochemical and spectroscopic investigations on copper and tin-lead alloys are in progress.

(7) As a model of atmospheric corrosion of metals, surface layers of iron and copper exposed to several kinds of corrosive gas mixtures are being investigated by using *in situ* spectroscopic techniques.

(8) The mechanisms of inhibition action of newly-developed benzotriazole derivatives are being explored for copper and copper alloys using electrochemical techniques. The effect of heat treatment on a minute-localized corrosion, "ant's nest corrosion", in copper tubes is also being studied under simulated conditions in order to more fully understand, and to further control, this type of corrosion in air-conditioning units.

(9) Investigations into the electrochemical behavior on aromatic thiols adsorbed on the surface of gold by FTIRAS continue.

Presentations

Effect of Dissolved Cations on Morphologies of Electrodeposited Al in Low-Temperature Chloride Melts Containing $AlCl_3$; M. Noguchi, S. Konda, T. Sasaki and T. Ishikawa: The 19th

Hokkaido Section Meeting of Electrochem. Soc. Japan, Sapporo, Jan., 1993.

Solubility of $TiCl_4$ in Equimolar NaCl-KCl Melts; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The 60th Annual Meeting of Electrochem. Soc. Japan, Tokyo, Apr., 1993.

Morphologies of Electrodeposited Metals in Several Chloroaluminate Melts Containing Metal Chlorides; M. Noguchi, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*

Tarnishing Prevention of Copper and Copper Alloys with Benzotriazole Derivatives; T. Notoya and T. Ishikawa: The 65th Spring Meeting of Japan Chemical Society, Tokyo, April, 1993.

On the Methods for Introducing Titanium Tetrachloride to NaCl-KCl Melts; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: 1993 Int. Symp. Molten Salt Chemistry and Technology, Honolulu, Hawaii, May, 1993.

Corrosion of Lead-Tin alloys in Sulfuric Acid; T. Sasaki and T. Ishikawa: The 183rd Meeting of Electrochem. Soc., Honolulu, Hawaii, May, 1993.

Oxidation Reaction of p-Mercaptophenol Adsorbed on Gold Electrodes as Studied by *In situ* Infrared Reflection Absorption Spectroscopy; T. Sasaki and T. Ishikawa: *ibid.*

Prevention of Spot-tarnishing on Copper and Copper Alloys with Benzotriazole and its Derivatives; T. Notoya and T. Ishikawa: *ibid.*

Identification of Corrosion Products in Atmospheric Environment by *In situ* Infrared Spectroscopy; M. Nakata, T. Sasaki and T. Ishikawa: The '93 Hokkaido Section Spring Meeting of JIM, Muroran, June, 1993.

State Changes of p-Mercaprophenol on Gold Electrodes with Potential Variations; S. Hara, T. Sasaki and T. Ishikawa: *ibid.*

Copper Corrosion in Degradated Oils; T. Notoya and T. Ishikawa: *ibid.*

Anti-tarnishing Effect of Benzotriazole and its Derivatives for Copper Products; T. Notoya, N. Sugii and T. Yamauchi; The 13th Meeting of Japan Rust Prevention Association, Tokyo, July, 1993.

Inhibition Action of Benzotriazole Related Compounds for Copper Corrosion ; T. Notoya and T. Ishikawa : The 1993 Summer Meeting of The Hokkaido Sections of Chemical Society of Japan, Kushiro, July, 1993.

Investigation of Adsorbed States of Aromatic Thiols and Its Changes with Potential Variations by *In situ* Infrared Reflection Absorption Spectrscopy ; T. Sasaki and T. Ishikawa : The 66th Fall Meeting of Chem. Soc. Japan, Nishinomiya, Sep., 1993.

Inhibition Effect of Benzotriazole Derivatives on Dissolution of Copper ; T. Notoya, T. Ishikawa, Guo-ding Zhou, N. Sugii and T. Yamauchi : *ibid.*

Analysis of Potential Drops in Chemical Cells of High-Temperature Melts ; S. Konda, T. Sasaki and T. Ishikawa : The '93 Fall Meeting of the Electrochem. Soc., Japan, Fukuoka, Oct., 1993.

In situ Infrared Reflection Absorption Spectroscopy for Study of Atmospheric Corrosion ; M. Nakata, T. Sasaki and T. Ishikawa : The 40th Symp. on Corrosion and Protection, Naha, Nov., 1993.

Corrosion Behavior of Tin-Lead Alloys in Sulfuric Acid ; T. Sasaki and T. Ishikawa : *ibid.*

Galvanic Corrosion of Steel-Copper Couple in Domestic Water at a Stagnant Condition ; T. Notoya and T. Ishikawa : *ibid.*

Galvanic Corrosion of Steel-Copper Couples in Fresh Water ; T. Notoya : The 33rd Meeting of Japan Copper and Brass Research Association, Osaka, Nov., 1993.

Codeposition of Al and Ti in Low-Temperarture Melts ; S. Konda, T. Sasaki, T. Ishikawa and N. Guo : The 25th Symposium on Molten Salt Chemistry, Kobe, Nov., 1993.

Investigation of High-Temperature Melts for Elecrorefining of Al ; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa : *ibid.*

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Prof. Dr. H. Tamura,
Lecturer Dr. H. Konno, Mr. I. Saeki
and Miss. M. Hashimoto

Students

A. Furusaki, A. Uchibo, K. Ohkita, R. Hata, T. Miyai, T. Abe,
K. Utaka, N. Ohkushi and K. Kuribayashi

Dr. Tamura was invited by IBA to The 8th International Battery Materials Symposium held in Brussels, Belgium, in May. In the same month, Dr. Konno joined The 183rd Meeting of the Electrochemical Society held in Honolulu, U.S.A.

The research programs in our laboratory are:

(1) Preparation and characterization of spinel type manganese oxide

A spinel type manganese oxide ($\square Mn_2O_4$) with vacancies ($\square$) was prepared by topotactic extraction of Li^+ with nitric acid from a spinel type $LiMn_2O_4$. The oxide incorporates Li^+ ions very specifically, accompanying reduction of lattice Mn(IV) ions. The rate of incorporation increases with the Li ion concentration, tending towards limiting values, while with pH it increases exponentially. A kinetic model was proposed by assuming that (1) the oxidation of an OH^- ion with the lattice Mn(IV) ion excites a vacancy and (2) the excited vacancy incorporates an Li^+ ion. The obtained rate equation explained the observed results well. Substitution of the lattice Mn ions with other cations and its effect on incorporation are being studied.

(2) Modeling of the adsorption of divalent heavy metal ions on hematite

The adsorption of divalent heavy metal ions (Pb^{2+}, Cu^{2+}, Co^{2+}, and Zn^{2+}) on hematite (α-Fe_2O_3) was studied. The amount of adsorption increases with the ion concentration and solution pH. The adsorption behavior was modeled by assuming that (1) heavy metal ions are adsorbed at acid-type surface hydroxyl sites on hematite (-OH(a)) through (1 : 1) and (1 : 2) cation-proton exchange reactions, i.e. "surface complex" formation and (2) each exchange reaction is steadily suppressed with the progress of ion exchange due to lateral interactions between the interphase species. The model well reproduces the observed results, and the adsorption affinity of ions was characterized with model parameters. A good correlation was found between the adsorption affinity of ions and the tendency of ions for hydroxo complex formation. This supports our model which assumes that the metal ion adsorption is due to the formation of coordination bonds by donation of electron pairs from the lattice oxide ions to the metal ion, similarly to the hydroxo complex formation.

(3) Purification of manganese(II) sulfate solutions for manganese dioxide preparation

Removal of Mg^{2+} ions from Mn(II) sulfate solutions was attempted with phosphate ions. Mg^{2+} ions precipitate as phosphates and excess phosphate ions can be removed as Fe(III) phosphate precipitate. However, it was found that considerable fractions of Mn(II) ions also precipitate as phosphates, and a further study is necessary.

(4) Formation of perovskite structure La(III)–Cr(III)–Mn(III) oxide films by spray pyrolysis

A novel synthesis method of $(La_{1-x}A_x)(Cr_{1-x}B_y)O_3$ [A=Ca(II) or Sr(II), B=Mn, Co and so on] was further developed to form thin oxide films on ceramics and metals. The method utilized ultrasonic spraying and pyrolysis. The $La(Cr_{1-x}Mn_x)O_3$ (x=0–1) films were formed and characterized by XRD, SEM, electric conductivity measurements, and so on. Further invesgations on the formation of both A and B sites substituted ones are in progress.

(5) Electrochemical formation of mixed films on metals

Cathodic deposition method to form gel-like thin films (less than 1 μm in thickness) on metals was developed, in which cathodic reduction of nitrate ions was used to control the surface pH of metals. The Al(III)-Y(III) mixed hydroxide films having Y(III) content up to 60% were formed on nickel or stainless steels. It was found, however, that high content of Y(III) in the films cannot be explained by simple precipitation equilibrium. After drying at 350°C, the films showed good preformance as protective oxide coatings under oxidizing atmosphere at elevated temperatures. Further investigation on the formation of Al(III)-Zr(IV), Ce(III)-Ce(IV), Zr(IV)-Y(III) films is in progress.

(6) New anodizing method of aluminum to improve physical and chemical properties of oxide films

A two step formation method of anodic oxide films on aluminum was developed. The process consists of first thin film formation on the aluminum materials and second anodizing in acid solutions. For example, (a) after the formation of Mo-containg film on aluminum by cathodic deposition, it was anodized in a sulfo-succinic acid solution, (b) after chromate film formation by dipping, anodizing in a sulfulic acid solution was carried out, and so on. By this process, hardness and abrasion resistance of anodic oxide films were markedly increased, and in the case of above example (b) resistance of above example (b) resistance to pitting corrosion was greatly improved. Further development of the process is in progress.

(7) Initial stage of the high temperature oxidation of Fe–Cr alloys

There are many works on the high temperature oxidation of Fe-Cr alloys. Many of them are concerned with the long time oxidation and the number of the work on the initial oxidation is limited. Study on initial oxidation is important since it may give information about the oxidation at much longer time and about operation of stainless steel production, especially descaling and annealing processes. In this work thin films grown on Fe-Cr alloys oxidized in 1 atm of oxidizing gas for 0 to 300s at 1273 K were analyzed with several methods (TLXRD, XPS, AES-SAM, FTIR-RAS, and FE-SEM), sensitive to the surface properties. Effects of atmosphere, temperature, impurity metals on initial oxidation have been made clear.

Presentations

Mechanism of Codeposition of Impurity Ions into Electrolytic Manganese Dioxide; K. Ishizeki, H. Tamura and R. Furuichi: The 19th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Sapporo, Jan., 1993.

Effect of Grinding on Solubility of Pyrite in Sulfuric Acid —Influence of Structural Strain—; K. Sasaki, M. Tsunekawa, M. Inagaki and H. Konno: The 1993 Annual Spring Meeting of Min. and Mat. Proc. Inst. Jpn., Tokyo, Mar., 1993.

Modeling of Ion Adsorption on Soil Components; H. Tamura and R. Furuichi: The 65th Annual Spring Meeting of Chem. Soc. Jpn., Tokyo, Mar., 1993.

Formation of $LaCrO_3$ Thin Films by Ultrasonic Spray Pyrolysis; A. Furusaki, H. Konno and R. Furuichi: The 60th Annual Meeting of the Electrochemical Society of Japan, Tokyo, Apr., 1993.

Formation of Mixed Oxide/Nitride Films on Titanium via Electrodeposition; H. Konno and R. Furuichi: *ibid.*

Incorporation of Impurity Metal Ions in Electrolytic Manganese Dioxide and Affinity of Ions for Manganese Dioxide Surfaces; H. Tamura, K. Ishizeki, M. Nagayama and R. Furuichi: The 8th Intnl. Battery Materials Symposium, Brussels, Belgium, May, 1993.

Cathodic Deposition of Al(III)-Y(III) Mixed Oxyhydroxide Films on Stainless Steels to Improve Resistance to High Temperature Oxidation; H. Konno, R. Segawa, R. Hata, I. Saeki and R. Furuichi: The 183rd Meeting of the Electrochemical Society, Honolulu, Hawaii, May, 1993.

The Effect of manganese on the initial oxidation of type 430 stainless steel; I. Saeki, H. Konno and R. Furuichi: Fusyoku-Bosyoku '93, Tokyo, May, 1993.

Ion Exchange Properties of Spinel-type Manganese Oxide; A. Uchibo, H. Tamura and R. Furuichi: The 1993 Summer Meeting of the Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., Kushiro, Jul., 1993.

Modeling of Co^{2+} Ion Adsorption on Hematite; K. Ohkita, H.

Tamura and R. Furuichi: *ibid.*

Analysis of Oxide Films on Stainless Steels and the Oxide/Alloy Interface Layer by XPS and XRD; H. Konno, I. Saeki and R. Furuichi: *ibid.*

Thermal Analysis of Iron Oxide Hydrates; R. Furuichi: Nuclear Chemiatry and Chemical Engineering Center, Tokyo, Jul., 1993.

Modeling of Ion Exchange Reactions; H. Tamura and R. Furuichi: The 42nd Annual Meeting of Jpn. Soc. Anal. Chem., Hiroshima, Oct., 1993.

Contamination of Electrolytic Manganese Dioxide; H. Tamura, K. Ishizaki and R. Furuichi: The 46th National Symposium on Colloid and Interface Chemistry, Tokyo, Oct., 1993.

Formation of Mixed Oxide/Nitride Films on Titanium by the Pyrolysis of Anodic Oxide Films; H. Konno. K. Utaka and R. Furuichi: The 88th Meeting of Surf. Finish. Soc. Jpn, Nagoya, Oct., 1993.

Improving Oxidation Resistance of Stainless Steels at Elevated Temperatures by Electrodeposited Al(III)-Y(III) Oxide Films; H. Konno, R. Hata, I. Saeki and R. Furuichi: The 40th Japan Corrosion Conference, Naha, Nov., 1993.

Formation of Lanthanum Chromite Films by Spray Pyrolysis; A. Furusaki, H. Konno and R. Furuichi: *ibid.*

Effect of Atmosphere on the Initial Oxidation of Type 430 Stainless Steel; I. Saeki, H. Konno and R. Furuichi: *ibid.*

Non-constancy of Selectivity Coefficients—Description and Prediction of the Amounts of Adsorbed Ions; H. Tamura and R. Furuichi: The 9th Symposium for Jpn. Assoc. Ion Exchange, Chiba, Nov., 1993.

Improving Resistance to High Temperature Oxidation of Alloys by Electrochemical Surface Modification; H. Konno: "Green Materials" Workshop at the Institute of Materials Research, Tohoku University, Sendai, Nov., 1993.

COMPOSITE MATERIALS PROCESSING AND EVALUATION LABORATORY

Prof. Dr. T. Narita, Assoc. Prof. Dr. K. Ohsasa,
Mr. Taumi and Mr. Tanaka

Students

T. Mitsueda, S. Kawamori, M. Noguchi, S. Hayashi, T. Sasaki,
T. Yoshioka, M. Narumi, S. Hata, M. Mukaihira,
K. A. Zaini, M. Nakano, T. Toyama, R. Masumoto,
T. Watanabe, M. Suzuki T. Motoyama

Dr. K. Ohsasa and Mr. J. Tanaka joined our laboratory as associate professor and technician on April 1st. Research associate Mr. Y. Tu from University of Science and Technology Beijing stayed as a visiting researcher from April and he is investigating on high temperature sulfidation of nickel-based alloys.

Professor Narita visited United Kingdom on April 18–27 to attend the International Symposium on Computer Methods and Experimental Measurements for Surface Treatments which was held in Southampton, and presented the paper on "Non-destructive evaluation of fracture strength of ion-exchanged glasses by acoustic microspectroscopy". Professor Narita and doctor course students, Mr. Mitsueda and Mr. Kawamori, attended the International Symposium on High-Temperature Metal Chemistry IV held in Honolulu on May 15–24, and Mr. Mitsueda presented a paper on "Coloring Behavior of Stabilized Zirconia in Reaction with Active Metal Solder" and Mr. Kawamori presented a paper on "Grain Boundary Sulfidation Behavior of Austenitic Stainless Steels". On May 15–24, Professor Narita and Mr. Yoshioka attended the 3rd IUMRS International Conference on Advanced Materials held in Tokyo on August 30–September 2, and presented two papers on "Sulfidation properties of Ti–Al intermetallic compounds at elevated temperatures in H_2S–H_2 atmospheres". Professor Narita visited Shenyang, China, to attend the 2nd Chinese-Japanese Symposium on Basis and Application of Interfaces Sciences which was held on October 15-18, and presented a paper on "An effect of creamic strength on fracture strength of ceramic-metal joints".

Professor R. Streiff from University of Provence, France and Professor K. Przybylski from Academy of Mining and Metallurgy, Poland visited our laboratory on September 2nd, and Associate Professor Dr Wang Fuhui from Institute of Corrosion and Protection, Shenyang, China, visited our laboratory on September 6-8.

The research programs in our laboratory are as follows:

(1) Ceramic-metal joining

Aluminium nitride and silicon nitride ceramics were joined to metals using active alloy solders such as Ni-Cu-Ti, Ag-Cu-Ti, and Ag-Cu-In-Ti, and the new bonding process was developed. Zirconia-metal joinings were investigated for development of SOFC.

(2) High-temperature sulfidation of alloys

Sulfidation properties of stainless steels, nickel alloys, and Ti-Al intermetallic compounds were investigated at relatively low sulfur pressures in H_2S-H_2 atmospheres.

(3) Ultrasonic Micro-Spectroscopy

Scanning acoustic microscope was used to determine the residual stress by making use of the principle concept basing on the measurement of SAW velocity and its change in stress. This novel method was successfully applied to the ceramic-metal joints, ion-exchanged glasses, and Ag-ion diffused layer in glasses.

(4) Coloration process of zirconia ceramics

Coloration process and its origin were investigated in order to avoid degradation of the zirconia ceramic-metal joints.

(5) Molecular dynamics simulation of grain boundary formation

Grain boundary structures of metals and alloys were investigated by molecular Dynamics Simulation in order to elucidate the properties of grain boundary in relation to the crystal orientation difference.

(6) Analysis of solidification path of multi-component alloy systems

The Solidification path of ternary alloys were investigated with the method of combining thermodynamic analysis and solute diffusion calculation. Changes in the solid and solute fractions in each phase were estimated, and the degree of microsegregation formed in the alloy at the end of the solidification was quantitatively predicted.

(7) Galvanizing process of steels by hot Zn–Al and Al–Si dippings

Galvanizing of steels was carried out by using Zn–Al and A–Si molten alloys, and optimum condition was investigated to make galvannealed layer having high corrosion resistance. The interface structure formed during dipping processes was evaluated by means of SEM, EPMA and XRD.

(8) Thermal barrier coating

Thermal barrier coatings of the NiCrAlY–Zirconia composite were prepared by using Plasma Spray Coating Method and their mechanical properties, microstructures and high temperature oxidation properties were investigated.

Presentations

Sulfidation Properties of Titanium-Aluminium Intermetallic Compounds; T. Yoshioka and T. Narita: Hokkaido Section Meeting of Japan Society of Corrosion Engineering, Sapporo, Jan., 1993.

Unidirectional Solidification of Monotectic Alloy under Micro-Gravity (Second report) —Micro Structure—; M. Kudoh, T. Noguchi, K. Ohsasa, Y. Takei and T. Soya: The 2nd Meeting on Ttilization of Short Time Micro-Gravity, Sapporo, Jan., 1993.

Behavior of Molten Metal at the Transition from 1g to Micro-Gravity Condition; T. Noguchi, M. Kudoh and K. Ohsasa: *ibid.*

Computer Simulation of Grain Structure Formation of Castings; K. Ohsasa and M. Kudoh: Workshop on Modeling for Welding Science, Cocoa Beach, Florida, Mar., 1993.

Grain Boundary Sulfidation Behavior of Fe–36%Cr–C Alloy; S. Kawamori and T. Narita: The 112th Annual Meeting of JIM, Yokohama, Mar., 1993.

Coloring Behavior of Stabilized Zirconia due to Applied Direct Current; T. Mitsueda and T. Narita: *ibid.*

Effect of Heat Treatment of Spark Plasma on Properties of Sintering Duplex Materials; H. Taumi and T. Narita: *ibid.*

Non-Destructive Evaluation of Fracture Strength of Ion-Exchanged Glasses by Acoustic Microspectroscopy; T. Narita and H. Umekawa: International Symposium on Computer Methods and Experimental Measurements for Surface Treatments, Southampton, U.K., Apr., 1993.

Grain Boundary Sulfidation Behavior of Austenitic Stainless Steels; S. Kawamori and T. Narita: International Symposium on High-Temperature Metal Chemistry IV, Honolulu, Hawaii, May, 1993.

Coloring Behavior of Stabilized Zirconia in Reaction with Active Metal Solder; T. Mitsueda and T. Narita: *ibid.*

Change in Heat Transfer Coefficient of Molten Metal under Micro-Gravity Condition; M. Kudoh, T. Noguchi and K. Ohsasa: The 122nd Annual Meeting of Japan Foundrymen's Society, Tokyo, May, 1993.

Morphology of Structure and Micro-Segregation for Fe-Mn Alloy; J. Tanaka, M. Kudoh, K. Ohsasa and I. Oda: The Meeting of Hokkaido Section of Japn. Inst. Iron and steel, Muroran, Jun., 1993.

Analysis of Solidification Path of Fe-Cr-Ni Ternary Alloy; M. Nakaue, K. Ohsasa and M. Kudoh: *ibid.*

Sulfidation Properties of Ti-Al Intermetallic Compounds at Elevated Temperatures in H_2S-H_2 Atmospheres; T. Narita and T. Yoshioka: The 3rd IUMRS International Conference on Advanced Materials, Tokyo, Aug., 1993.

Application of Molecular Dynamics Method for the Research of the Grain Boundary Strength; K. Ohsasa: The Meeting of the Ferrous Materials and New Materials Research Group in The Hokkaido Section of ISIJ., Muroran, Aug., 1993.

Sulfidation Properties of Titanium-Aluminium Intermetallic Compounds at 1173K in H_2-H_2S Atmospheres; T. Yoshioka and T. Narita: International Symposium on High Temperature

Materials at Solve Global Environmental Problems, Tokyo, Sep., 1993.

Structure and Segregation Behavior of Fe-Mn Alloy; J. Tanaka, M. Kudoh, K. Ohsasa, T. Narita and I. Oda: The 113th Annual Meeting of JIM, Nagoya, Oct., 1993.

Prediction of the Property of Solid-Liquid Coexisting Zone Based on Percolation Model; K. Ohsasa, J. Yokota, M. Kudoh and T. Narita: *ibid.*

Analysis of Non-Equilibrium Solidification of Fe-Cr-Ni Ternary Alloy :M. Nakaue, K. Ohsasa and M. Kudoh: *ibid.*

Thermocycle Behavior of Hot Corrosion Resistance of NiCrAlY Sprayed Coating; H. Taumi, M. Narumi and T. Narita: *ibid.*

Physico-Chemeical Properties of MCrAlY Sprayed Coating; H. Taumi and T. Narita; *ibid.*

On Improvement for Atmospheric Resistance of Ceramic/Metal Joints (On Improvement of Anti-Corrosion Properties of Cceramic-Metal Joints); S. Hayashi and T. Narita: *ibid.*

An Effect of Ceramic Strength on Fracture Strength of Ceramic-Metal Joints (On the Effect of Ceramic Strength on Ceramic-Metal Joints); S. Hata and T. Narita: *ibid.*

Measurement of Cation Distribution in the Sulfide Scale Formed on Fe-Cr Alloy; M. Noguchi and T. Narita: *ibid.*

Reaction Behavior of Stabilized Zirconia/Cermet Interface; T. Mitsueda and T. Narita: *ibid.*

Effect of Ti or Nb Addition on Grain Sulfidation of Fe-Cr Alloy; S. Kawamori and T. Narita: *ibid.*

Thermal Cycle Behavior of Hot Corrosion Resistance of NiCrAlY Sprayed Coating; M. Narumi, H. Taumi and T. Narita: *ibid.*

An Effect of Ceramic Strength on Fracture Strength of Ceramic-Metal Joints; T. Narita and S. Hata: The 2nd Chinese-Japanese Symposium on Basis and Application of Interfaces, Shenyang, China, Oct., 1993.

Solidified Structure of Zn-Pb Alloy under Micro-Gravity Condition; M. Kudoh, T. Noguchi, K. Ohsasa, Y. Takei and T. Soya: The 123th Annual Meeting of Japan Foundrymen's Society, Takaoka, Oct., 1993.

Localized 'Ant Nest' Corrosion of Copper Tubing and Preventive Measures

Takenori Notoya

MATERIALS PERFORMANCE,
32, [5], 53-57 (1993).

An unusual form of copper tube corrosion has been detected early in service and in leakage tests after manufacturing. The morphology of this corrosion is similar to an ant nest when viewed in cross section. Cases of the premature failure of copper tubes, simulation tests, corrosion mechanisms, and preventive measures are discussed. (English)

Corrosion Inhibition of Copper by 2-Mercaptobenzothiazole and Benzotriazole in Low-Conductivity Solutions

Guo-ding Zhou, Yiqi Feng, Yiping Wu, Takenori Notoya,
and Tatsuo Ishikawa

Bull. Chem. Soc. Jpn., **66**, 1813–1816 (1993).

Corrosion inhibition of copper in a low-conductivity medium ($<10\ \mu S\ cm^{-1}$) containing benzotriazole (BTA) and/or 2-mercatobenzothiazole (MBT) was studied by using the AC impedance technique, Auger electron spectroscopy and corrosion tests. As the MBT concentration increased, the corrosion rate of copper abruptly rose to a peak, rapidly fell, and then finally decreased steadily. The maximum corrosion rate appeared at a MBT concentration of about 0.5 ppm. However, a concentration of more than 1.5 ppm MBT could effectively inhibit copper corrosion. The results from AC impedance measurements agreed with those from corrosion tests. The film resistance could be observed only when the MBT concentration was in excess of 1.5 ppm. A combination of BTA and MBT proved to be more effective than either compound used alone. (English)

Prevention of Surface Tarnishing of Copper Alloys with Benzotriazole and its Derivaties

T. Notoya

Journal of the Japan Copper and Brass Research
Association, **32**, 45–50 (1993).

Benzotriazole (BTA) is one of the most effective corrosion inhibitors for copper and copper alloys and has been widely used for more than 40 years. Although the BTA-treated copper base materials retain a stain-resistant property in most environments, the staining problem of copper products occurs during storage or transportation mostly during wet seasons. Excessive protection with BTA, however, has an undesirable effect on the subsequent processes such as plating, soldering, wire-bonding and artificial patination. Eight different inhibitors including four newly-developed BTA derivatives were used to evaluate their effectiveness in preventing copper surface tarnishing. The inhibitors include Chromic acid (CrO_3), Benzotriazole (BTA), Dihydroxypropyl-benzotriazole (BTA-GL), 2, 3-Dicarboxypropyl-benzotriazole (BT-250), [1, 2, 3-Benzotriazoly-1-methyl] [2-ethylhexyl] amine (BT-341), Bis[(1-benzotriazolyl) methyl]phosphonic acid (BTA-PA), 3-Amino-1, 2, 4-triazole (ATA) and N-cyclohexyldiethanolamine (Wandamin). After pretreatment with a solution containing 10 ppm chloride ions in the absence of inhibitors, the tarnish density increased in the order of phosphorous deoxidized copper < phosphorous bronze < Beryllium copper. After an 8-day exposure period it was 0.42, 1.31 and 1.94/mm^2 for PD copper, P bronze and B copper, respectively. The number of tarnished spots dramatically dropped to the order of 0.01/mm^2, independent of the materials, when the sample was pretreated with 1 mM inhibitor solution containing 10 ppm chloride ions. The morphology of the tarnished spots developed in the inhibitor-treated surfaces were rather irregularly shaped and dark in color. From the exposure test, the most suitable inhibitors to

prevent spot-tarnishing were BTA and BTA-PA for PD copper, BTA-PA for P bronze, and BTA and BTA-GL for B copper. (Japanese)

Inhibition Effect of Benzotriazole Phosphonic Derivative on Dissolution of Copper

T. Notoya, N. Sugii and T. Yamauchi

BOUSEI KANRI, **37**, [5], 15 (1993).

Inhibition action of Bis [1-benzotriazolyl] methyl phosphonic acid as a corrosion inhibitor for copper was evaluated by immersion tests in 3% NaCl solution. This BTA-derivative showed excellent inhibition for copper corrosion. The effectiveness of the BTA-derivative was almost the same as that of benzotriazole. The anodic complex film formed on copper surface was compact, and thus more protective. (Japanese)

Effect of Niobium Doping on the Atmospheric Oxidation of Fe-Si-Al Magnetic Alloys

Hidetaka Konno, Shin-ichi Matsugi, Isao Saeki,
Ryusaburo Furuichi and Toshiya Nishimura

Corr. Sci., **35**, 727-734 (1993).

Magnetic alloys having a composition around Fe-10Si-5Al are called "Sendust". Doping with high valence metal elements, such as titanium, vanadium, zirconium and niobium, is considered to be effective in improving the corrosion resistance of Sendust, but systematic data have not been reported. In the present work, the effect of niobium doping on the atmospheric oxidation of Sendust was studied with XPS and ellipsometry. In air with a relative humidity (RH) of 42.8-90% at 80°C, oxide films grew rapidly on both doped and undoped Sendust in the initial 2 days. After 20 days, the thickness reached 5-6 nm with mirror finished specimens (by ellipsometry), thinner than on pure iron (*ca* 7 nm). The films were thicker on specimens polished with No. 600 emery paper (by XPS). The films were estimated to be a mixture of silica-alumina composite oxides and Fe(III)-oxyhydroxides. With RH=42.8% (no condensed water on the surface), the proportions of Si(IV) and Al(III) in the film were larger with the niobium doped Sendust than with the undoped Sendust. This suggests that a small amount of niobium doping may improve the corrosion resistance of Sendust in a dry atmosphere. With RH=90% (with condensed water on the surface) the film composition did not show a significant difference with doping, in agreement with the results of anodic polarization experiments, indicating that under wet conditions no doping effect may be expected. (English)

Observation of Pitting Behaviour of Iron by Spectrum Analysis of Current Fluctuation

Tadahiko Mizuno and Masatoshi Kitaichi

DENKI KAGAKU, **61**, [5], 589–593 (1993).

Pitting initiation and growth behaviour has been observed by spectral analysis method of anodic current fluctuation for the pure iron using low noise potentiostatic circuit. The relationship between stability of the iron and spectrum of current fluctuation can be established by the inclination of spectrum. White spectrum showed a stable state of iron in the passive region while the spectrum having some inclination an unstable one. Especially, the spectrum showed increase of inclination just before occurrence of pitting corrosion. It means that the method has a possibility of the expectation of the localized corrosion occurring. (Japanese)

The Effect of Applied Stress and Potential on Corrosion Fatigue Behavior of SiC/7075 Al Metal Matrix Composite

Kazuhiko Noda and Tooru Tsuru

Zairyo-to-Kankyo, **42**, 641–647 (1993).

In the NaCl solution, 4 points bending tests were attempted to investigate the corrosion fatigue behavior of SiC/7075 Al metal matrix composite (MMC) comparing with ordinary matrix Al alloy (Al alloy). Time to failure of both MMC and Al alloy decrease with an increase of loaded stress of applying at more anodic potential, and under the same condition, corrosion fatigue life of MMC was longer than that of Al alloy. The crack initiation and growth in corrosion fatigue process explained by passive region, repassivation process, and dissolution of newly created surface can be monitored by measuring the potential at the open circuit and the current at the potentiostatic condition. As the results of this technique, it was shown that corrosion fatigue process, fracture morphology, and the site of the crack initiation for MMC was different from them for Al alloy, and the crack occurred from the bottom of pits on the MMC. Current amplitude corresponded to the defect of corrosion fatigue. According to the measurement of current amplitude, it was shown that once corrosion fatigue started, MMC got marked damage, however for almost all the period of corrosion fatigue test, it was resistive. (Japanese)

On the Methods of Introducing Titanium Tetrachloride to NaCl-KCl Melts

Takehiko Kumagai, Shoichi Konda, Takeshi Sasaki
and Tatsuo Ishikawa

Proc. Molten Salt Chemistry and Technology,
1, 265-275 (1993).

For the production of titanium alloys from high temperature molten salts containing $TiCl_4$ as a raw material, methods for introducing $TiCl_4$ to NaCl-KCl melts were investigated. With a method directly introducing $TiCl_4$ gas, three kinds of lances were examined in terms of the contact time and contact area of gaseous $TiCl_4$ with the solvent melts. The results show that $TiCl_4$ introduced through helical and porous lances dissolved nearly four times as quickly as that introduced through a straight lance. It takes 7 hours to reach 2.27 mol % $TiCl_4$ through the porous lance. With the addition of K_2TiCl_6 preliminarily synthesized from KCl and $TiCl_4$ to NaCl-KCl mixtures only 10 minutes was needed to achieve 6.5 mol % $TiCl_4$ melts. (English)

Cathodic Depositon of Al (III)-Y (III) Mixed Oxyhydroxide Films on Stainless Steels to Improve Resistance to High Temperature Oxidation

Hidetaka Konno, Rina Segawa, Ryusaku Hata,
Isao Saeki and Ryusaburo Furuichi

Proc. Symp. Corrosion Protection by Coatings and Surface
Modification, p. 66-77, The Electrochemical
Society, Pennington, N. J. (1993).

A cathodic deposition method to form Al (III)-Y (III) mixed oxyhydroxide films from nitrate solutions was developed. The method utilizes the pH increment at cathode surface caused by cathodic reduction of nitrate ions. The formed films were gel-like and adhesive to nickel or stainless steel substrate. The equilibrium calculations for solubilities of Al (III) and Y (III) species suggested that the Y (III) content in the film will be very low, but experimental results were reverse. For example, average composition of the film formed on type 430 SS in 0.006 mol/L $Al(NO_3)_3$-0.30 mol/L $Y(NO_3)_3$ at -0.7 V (SCE) was $[Al(III)]_f \sim 13$ mmol/m^2, $[Y(III)]_f \sim 17$ mmol/m^2. The film extremely decreased the oxidation rate of stainless steels at 1000°C in a 0.20 atm H_2O-air atmosphere, e.g. the mass gain of coated type 430 specimen was 1.7 g/m^2 after 22 h, which corresponds to $k_p'' = 4 \times 10^{-5}$ g^2/m^4 s. (English)

Anodizing of ADC12 Aluminum Die-Casting Alloy
—Effect of Alloying Elements and Preparation Method on the Film Formation—

Hideaki Takahashi, Kohta Shiga, Keiichi Watanabe
and Masahiro Seo

J. Surface Finishing Soc. Jpn., 44, 542-548 (1993).

The anodizing of ADC12 aluminum die-casting alloy, ADC12 without Cu, Fe, or Mn (M-ADC12), cast ADC12 (C-ADC12), and rapidly solidified ADC12 (RS-ADC12) has been investigated in 10 and 30 wt % H_2SO_4 solutions at 293 K with a constant current density of 100 A/m^2. Anodic oxide film formation was examined by measuring the time variations in anode potential, the amount of dissolved Al^{3+}, Cu^{2+} and Fe^{2+} ions, and the volume of O_2 evolved on the anode, as well as by electron microscopic observation of the oxide film.

The steady value of the anode potential in 10 wt %-H_2SO_4 solution was 35-57 V, increasing in the order C-ADC12$\ll$RS-ADC12$=$M-ADC12$<$ADC12. The metal dissolution current was 22-25 A/m^2, independent of the kind of specimen, while the gas evolution current was 15-30 A/m^2, increasing in the order M-ADC12$\ll$RS-ADC12$=$C-ADC12$<$ADC12. Increases in acid concentration caused decreases in the anode potential and gas evolution rate.

The difference in the anode potential and gas evolution rate during anodizing are discussed in terms of the inhibition of ion transport and acceleration of electron transport across the barrier layer, due to the formation of composite oxide, Al(Si, Cu, Fe)Ox. (Japanese)

Metallizing of Silicon-Carbide Ceramics with Manganese Vapor

Toshiyuki Takashima, Tsuyoshi Yamamoto
and Toshio Narita

Jounal of the Ceramic Society of Japan,
101 [2], 164-168 (1993).

Silicon-carbide ceramic were metallized with manganese by the vapor-diffusion method. Pure manganese powder as a vapor source was used to metallize SiC ceramics at 923 K to 1223 K for up to 90 ks in a dynamic vacuum atmosphere. The structure and composition of the metallized layers were investigated by scanning electron microscopy, electron-probe microanalysis, and X-ray diffraction analysis. At the initial stage of the metallization, manganese vapor reacted preferentially with the carbon in the grain boundaries of SiC ceramics to form a manganese carbide, and then a metallized layer with four sub-layers was formed. The four-sublayers were composed of manganese carbide ($Mn_{23}C_6$) at the surface layer, a mixture of ternary compound (Mn_8Si_2C) and manganese carbide ($Mn_{23}C_6$) in the outer layer, manganese silicide (Mn_5Si_2) at the middle layer, and a mixture of ternary compound (Mn_8Si_2C)and SiC particles at the bottom layer. Growth of the metallized layer with the four-sublayer structure obeyed the parabolic law at the initial stage, and then slowed down due to the formation of the manganese carbide layer ($Mn_{23}C_6$) on the top surface. The parabolic rate constants (k_p) for the growth of metallized layers were 10^{-16}-10^{-13} $m^2 \cdot s^{-1}$ at 1073-1223 K. The activation energy for the growth of metallized layers (Q_{kp}) was 225 $kJ \cdot mol^{-1}$. (English)

Effect of Preparation Temperature and Grinding Time of α-Fe_2O_3 on its Reactivity for $MgFe_2O_4$ Formation

Ryusaburo Furuichi, Syuuichi Nakano, Shiro Shimada
and Tadao Ishii

Solid States Ionics, **63-65**, 195-200 (1993).

α-Fe_2O_3(500) and α-Fe_2O_3(1200) were prepared at 500°C and 1200°C, and ground for $t_m=0$-300 min. The BET area (S_{BET}), median diameter (D_m), and crystallite size (D_c) of α-Fe_2O_3(500) were unchanged with t_m, but α-Fe_2O_3(1200) showed increasing S_{BET} and decreasing D_c. $MgFe_2O_4$ formed through surface reaction followed by the process obeying Jander's law. Grinding increased the fractional surface reaction. Jander's rate was constant for α-Fe_2O_3 500) and increased with t_m for α-Fe_2O_3(1200). (English)

A Solid-Liquid Diffusion Couple Study of a Peritectic Reaction in Iron-Carbon System

Kiyotaka Matsuura, Youichi Itoh and Toshio Narita

ISIJ International, **33** [5], 583-587 (1993).

δ-iron and melted high carbon steel with carbon contents of the solvus and liquidus lines, respectively, in an iron-carbon equilibrium phase diagram, were held in contact with each other at 1696 K. The thickness of the γ-phase formed between the δ-phase and the liquid phase was measured. The relationship between the thickness x (μm) and the holding time t (s) was found to be $x = 85.7\,t^{0.50}$.

The distribution of the carbon concentration over those three phases was also measured. The results showed a steep gradient of the carbon concentration in the γ-phase and an equilibrium conjugation relationship at both the δ/γ and γ/liquid interfaces

These findings regarding the growth rate of the γ-phase and the distribution of the carbon concentration were both good agerement with the results of a simulation of the peritectic reaction based on a diffusion-controlled mechanism. (English)

Effect of Strain on Ferrite Transformation from Super-cooled Austenite in Fe-0.5%C Alloy

Kiyotaka Matsuura, Youichi Itho and Toshio Narita

ISIJ, **79**, 968-972 (1993).

Fe-0.51 wt%C alloy was cooled from 1000°C at 0.3°C/s and rooled at 710°C, at which austenite was super-cooled by 55°C. The isothermal transformation behavior at 710°C from the super-cooled and strained austenite to ferrite was investigated. It has been found that the nucleation rate of the ferrite particles increases with strain and that the rate constant for the growth of the ferrite particles remains constant regardless of the strain. The time required for the transformation and the average size of the ferrite particles decrease with increasing strain. (Japanese)

Effect of Rolling Temperatures on the Deformation Texture of Hypo-eutectic Mg-Li Alloy

Youichi Itoh, Kiyotaka Matsuura, Hiroshi Taumi,
Noboru Yonezawa and Toshio Narita

Bulletin of the Faculty of Engineering Hokkaido
University, No. 162, 203-211 (1993).

Hot-extruded flat bars of hypo-eutectic Mg alloy containing 6.3 mass% Li were rolled at 230 K, 300 K, 420 K and 520 K, and the deformation textures for Mg-rich phase, which had possessed on h.c.p lattice, were investigated.

The texture for a sheet rolled at 230 K was composed of two components. The predominant component was $(0001)\langle 11\bar{2}0\rangle$ and $(0001)\langle 10\bar{1}0\rangle$ rotated ±15-20° about a transverse direction and the subsidiary component was $(0001)\langle 10\bar{1}0\rangle$ rotated ±30-40° about a rolling direction. As the rolling temperature rised, the former component became gradually weak, while the latter component about rolling direction became strong and approached to an orientation $\{11\bar{2}0\}\langle 10\bar{1}0\rangle$.

It is supposed from the above results that active deformation mechanisms are changed from (0001) slip and $\{10\bar{1}2\}$ twin at low temperature to $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ slips at high temperature.
(Japanese)

Large Undercooling due to Oxide Flux in Plain Carbon Steel

Masayuki Kudoh, Jun-ichi Tanaka, Kohjiroh Okuyama
and Ken-ichi Ohsasa

Bulletin of the Faculty of Engineering Hokkaido
University, No. 162, 191-202 (1993).

In this study, a new flux for achieving high undercooling in plain carbon steel was developed. The flux was made by mixing of Al_2O_3, SiO_2 and CaO. Carbon steel weighing 100 g, was inserted into an alumina crucible and covered with the flux, was melted and frozen with a slow cooling rate. Then, it could be statically undercooled and the undercooling in the carbon steel was changed with the flux composition. In this experiment, carbon steel was cooled down to 232 K by using the flux of $14\%Al_2O_3$-$57\%SiO_2$-$29\%CaO$. The microsegregation abruptly reduced to below the undercooling of around 50 K resulting from the rapid increase in partition coefficient, and the hardness profile in the plain carbon steel undercooled till 213 K was uniform according to a short period from the start to end of the solidification. It is considered as a mechanism to obtain high undercooling that alumina inclusions are eliminated from molten steel to the flux and that soluble oxygen in the molten steel is decreased with reduced Si from SiO_2 in the flux. (Japanese)

Refining Mechanism of Primary Crystals in Hypereutectic Al-Si Alloy Ingots by the Duplex Casting Process

Tatsuya Ohmi, Yasuhiro Tanaka, Masayuki Kudoh
and Ken-ichi Ohsasa

Bulletin of the Faculty of Engineering Hokkaido
University, No. 162, 173–183 (1993).

Recently, the authors reported the refinement of primary silicon crystals in the hypereutectic Al–22mass%Si alloy ingots produced by the Duplex Casting process with the combination of Al–12mass%Si alloy as the first melt and Al32mass%Si alloy as the second melt. In this study, three possible origins of the refined primary crystals were examined: (1) detachment of eutectic silicon crystals during the remelting process of solidified shell of the first melt, (2) nucleation in the second melt during the mixing process of the first and second melts, and (3) nucleation after complete mixing.

In order to examine the first origin, two combinations of alloy compositions were selected for the Duplex Casting process; (a) Al–33mass%Cu and Al–32mass%Si; and (b) Al and Al–44mass%Si. As a result, the primary silicon crystals were refined even though the first melt was free from silicon in either case. Therefore, the first origin is concluded to be not dominant in the refinement of primary crystals.

The combination of Al–51mass%Ge alloy and Al–32mass%Si alloy was selected to examine the second and third origins. The germanium concentration in the refined primary crystals was lower than the possible minimum concentration predicted on the assumption that the primary crystals came from the third origin. Therfore the second origin, i. e. nucleation in the second melt, is confirmed as the predominant one.

Based on these results, a refining mechanism of primary crystals by the Duplex Casting process is presented. (Japanese)

Affinity of Lithium Ions for Surface Hydroxyl Groups on Manganese Dioxide Samples

H. Tamura, A. Uchibo, N. Katayama, M. Nagayama
and R. Furuichi

Progress in Batteries & Battery Materials,
12, 151-156 (1993).

The amount of lithium ions adsorbed on manganese dioxide samples (IC12, 22) was measured as a function of pH by acid-base titration, and it was compared with other alkali metal ions. The adsorption is ion exchange between cations and protons of acid hydroxyl sites on the oxides, and it increases with pH. At high pH (high coverage), the amount of adsorption was in the order: $Li^+ > Na^+ > K^+ > Cs^+$. The adsorption behavior of ions was analysed with our model, analogous to the Frumkin isotherm, where suppression of adsorption by lateral interactions between adsorbed ions is considered. It was found that both the intrinsic affinity of ions for adsorption and the lateral repulsion between adsorbed ions increase with the atomic number of alkali metal ions (opposite order as above). This suggests that alkali metal ions are adsorbed as hydrated ions, since the hydrated radius and hence the site-ion and ion-ion distances decrease in this order. With increasing coverage, Li^+ ion with lower affinity is more highly adsorbed due to lower repulsion than the other ions with higher affinity and higher repulsion. (English)

Modeling the Ion-Exchange Adsorption of Heavy Metal Ions on the Surface of Metal Oxides

Hiroki Tamura, Noriaki Katayama
and Ryusaburo Furuichi

Bunseki Kagaku, 42, 719-724 (1993).

The ion-exchange adsorption of heavy metal ions (Cu^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+}) on metal oxides (MnO_2, Fe_3O_4, and Al_2O_3) was modeled so as to enable a description and prediction of the amount of adsorption as a function of the ion concentration, exchange-site density, and solution pH. The model assumes that heavy metal ions are adsorbed through (1 : 1) and (1 : 2) ion-exchange reactions with the protons of the acid-type surface hydroxyl groups on metal oxides (-OH(a)), and that each exchange reaction is steadily suppressed along with the progress in ion exchange due to electrostatic lateral interactions between the species in the solid/solution interphase. The equilibrium conditions of the (1 : 1) and (1 : 2) exchange reactions are given by: $K_1^\circ = K_1 \exp(B_1\theta_1)$ and $\beta_2^\circ = \beta_2 \exp(B_2\theta_2)$, where K_1° and β_2° are the equilibrium constants, K_1 and β_2 the concentration ratios, B_1 and B_2 the suppression constants, and θ_1 and θ_2 the coverages of the exchange sites. The values of K_1°, β_2°, B_1, and B_2 were determined by fitting the model equations to the experimental adsorption isotherms. With the established constants the fractions of adsorbed ions were calculated as a function of the pH for given concentrations of added metal ions and metal oxides. From the calculations, the adsorption affinity order of ions for MnO_2 is $Cu^{2+} > Mn^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+}$, and the Co^{2+} adsorption ability order of oxdes is $MnO_2 > Fe_3O_4 > Al_2O_3$. (Japanese)

Polyfunctionality of Resin Carboxyl Sites in Ion Exchange with Alkali Metal Ions

Hiroki Tamura, Masashi Kudo and Ryusaburo Furuichi

Anal. Chim. Acta., **271**, 305-310 (1993).

The ion-exchange behaviour of a weak acid-type cation-exchange resin with alkali metal ions was obtained as a function of pH by titration. The behaviour was analysed with a model that assumes that the resin has two types of carboxyl sites (I and II) with different reactivities (polyfunctionality) and that the ion exchange at each site in the solid/solution interphase. The ion-ex change parameters in the model were determined by multi-parametric curve fitting. The values indicate that the type I sites are much more reactive than the type II sites and are more subject to suppression. The polyfunctionality was ascribed to the micropore structure of the resin : the type I sites are distributed in wider pores where hydrated ions are adsorbed electrostatically with larger lateral interactions and the type II sites in narrower pores where dehydrated ions are adsorbed by forming coordination-type chemical bonds with smaller lateral interactions. The activity coefficients of interphase species are discussed in terms of the electrostatic lateral interactions between these species. (English)

Decommissioning of Nuclear Reactor

M. Ishikawa, S. Yanagihara, T. Kozaki
and M. Tachibana

Kodansha, April, 1993, ISBN4-06-206419-7.

The Japan Power Demonstration Reactor (JPDR) decommissioning program was begun in 1981 by the Japan Atomic Energy Research Institute (JAERI) under contract with the Science and Technology Agency (STA).

This book describes the actual dismantling of the JPDR and the related development of reactor decommissioning technology as well as decommissioning activities in other countries. (Japanese)

Cold Fusion Reaction Products and Behaviour of Deuterium Absorption in Pd Electrode

Tadahiko Mizuno, T. Akimoto, K. Azumi and M. Enyo

Frontiers Science Series No. 4, 373-376 (1993).

Excess heat generation from Pd electrode during cathodic polarization in D_2O-LiOD solution was investigated as a function of D/Pd loading ratio. The excess heat was observed when a Pd sample was filled with deuterium to D/Pd=0.90 by cathodic charging. The excess heat (H_{ex}) increased with D/Pd in an exponential manner; the H_{ex} was of the order of magnitude of 0.1 watt/cm^2 at D/Pd=1.0. (English)

Diffusion and Permeation of Hydrogen/Deuterium in Palladium Electrode

Kazuhisa Azumi, T. Fujita, T. Mizuno and M. Seo

DENKI KAGAKU, **61**, 576, [5] (1993).

Electrochemical properties of palladium electrode in electrolytes of light/heavy waters, permeation efficiency and diffusion behaviors of hydrogen/deuterium through palladium were investigated. From potential change of Pd electrode during hydrogen/deuterium charge and polarization curves after charging, growth rate of β-phase is higher in heavy water than in light water. The rate of hydrogen/deuterium absorption into palladium in acidic solution is higher than in alkaline solution. By using AC modulation technique diffusion coefficients of hydrogen D_H and deuterium D_D were evaluated as a function of temperature and charging time. At lower charging current, D_H increases with charging time, probably due to filling trap states in Pd. On the other hand, at higher charging current, D_H decreases with charging time. This result can be explained by formation of a new phase with high H/Pd ratio at Pd surface in which D_H is smaller than that in the α or β-phase. (Japanese)

Acoustic Emission from a Palladium Electrode during Hydrogen Charging and Its Release in a LiOH Electrolyte

Kazuhisa Azumi, Shukuryou Ishiguro, Tadahiko Mizuno
and Masahiro Seo

J. Electroanal. Chem., **347**, 111–121 (1993).

Acoustic emission (AE) from a palladium electrode dipped in a 0.1 M LiOH electrolyte was measured during electrochemical hydrogen charging and its release. Large AE signals were observed for a few minutes in the first stage of the hydrogen charging in contrast with the small random AE signals caused by the evolution of hydrogen and oxygen gas. These signals appear to reflect the deformation of the Pd lattice by hydrogen charging. Various types of periodic AE signals were slso observed during hydrogen charging and hydrogen release after charging for long periods. It is believed that these phenomena are associated with the hydrogen-transfer through defects existing in the palladium. (English)

Band Shifts of IR Spectra of Aromatic Thiols Adsorbed on Gold Electrodes with Potential Changes

Takeshi Sasaki and Tatsuo Ishikawa

DENKI KAGAKU, **61**, 814-815 (1993).

Band shifts with electrode potential of aromatic thiols adsorbed on gold polycrystalline electrodes were investigated by in-situ IRAS experiments.

The experimental results on p-mercaptophenol and 4-methoxybenzenethiol showed that C-O and C-O-C vibrational frequencies shifted with potential changes, though the skeletal vibrational frequencies of benzene ring depended little on them. This frequency behavior demonstrates that the effects of electrode potential changes appeared stronger on the bands farther from the electrode surface and provides a clue to the reason for the band shift mentioned above. (English)

Thermal Analysis of Hydrous Iron Oxides as the Corrosion Products of Steels

Ryusaburo Furuichi

Zairyo-to-Kankyo, **42**, 322–330 (1993).

Applications of thermoanalytical techniques of DTA, TG and DSC were described to show inhibitory effects of the added foreign metal ions on α-FeOOH formation during aging of amorphous ferric hydroxide precipitates and α-Fe_2O_3 formation by heating of the hydroxides. The metals used were Cu, Co, Mg, Zn, Cr, and Al, which were added to the hydrous oxides by co-precipitation method. Gel-mixing and mortar-mixing of $Cu(OH)_2$ and CuO were tried and showed that the former resulted in a similar inhibitory effect to the co-precipitation method and the latter was less inhibitory. Oxidation temperature for $Fe_3O_4 \rightarrow \gamma$-$Fe_2O_3$ and transition temperature for γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ were also observed to change with the foreign metals added to Fe_3O_4 precipitates. (Japanese)

X–Ray Photoelectron Spectroscopy (XPS)

Hidetaka Konno

Zairyo-to-Kankyo (Corr. Engr.), **42**, 27–36 (1993).

Application of X-ray photoelectron spectroscopy (XPS) to corrosion science was introduced in both qualitative and semiquantitative aspects. In particular, abilities and limitations as a surface analytical techique were explained with practical examples.
(Japanese)

Leaching Behavior and Surface Characterization of Pyrite in Bacterial Leaching with *Thiobacillus ferrooxidans*

Keiko Sasaki, Masami Tsunekawa, Hidetaka Konno,
Tsuyoshi Hirajima and Takakatsu Takamori

Shigen-to-Sozai (J. Min. Mat. Process. Inst. Japan),
109, 29–35 (1993).

Bacterial leaching tests of pyrite with *Thiobacillus ferrooxidans* were performed, and leaching solutions and pyrite surfaces were analyzed during the tests.

The leaching of pyrite mainly proceeded according to the indirect bacterial leaching mechanism. The main reactions in this mechanism, i.e. the enzymatic oxidation of ferrous iron and sulfur by *T. ferrooxidans* and the chemical oxidation of pyrite by ferric iron, accelerated when the number of the bacteria increased logarithmically. With the rapid increase in the concentrations of ferric iron and sulfate in the leacing solutions, insoluble sulfate compounds were precipitated on pyrite. The redox-potential (Eh) was dependent on the mole ratio, $[Fe^{3+}]/[Fe^{2+}]$ in the leaching solutions. The redox-potential increased in the active phase of bacteria and decreased in the latter inactive phase. It indicates that Eh can be a measure of the activity of *T. ferrooxidans* in the leaching process as reported by others. In the latter inactive phase, the insoluble sulfate compound formed on pyrite was shown to be jarosite by FTIR and XPS. (Japanese)

Piezoelectric Response to Changes in Surface Stress of a Palladium Electrode in Perchloric Acid Solution Containing Chloride Ions

Masahiro Seo and Masaki Aomi

J. Electroanal. Chem., **347**, 185-194 (1993).

The interfacial properties of a palladium electrode in 0.1 mol dm^{-3} perchloric acid solution containing chloride ions were investigated from the piezoelectric response of changes in surface stress induced by potential modulation. It was found from the piezoelectric signals that the potential of electrocapillary maximum E_{max} or potential of zero charge (pzc) is present in the potential region of hydrogen absorption into palladium. The pzc shifted linearly toward the negative direction with an increasing logarithm of chloride ion concentration i.e. the Esin-Markov relation held between the pzc and chloride ion concentration, indicating specific adsorption of chloride ions on the palladium surface.

Furthermore, the piezoelectric signals indicated that sign reversal of the surface charge took place in the potential range of oxide formation and reduction. The sign-reversal of the surface charge was attributed to structural changes of the palladium surface associated with oxide formation and reduction. The potentials at which the sign-reversal of the surface charge took place during cathodic reduction of oxide shifted toward the positive direction with increasing chloride ion concentration. The effects of chloride ions on the sign-reversal of the surface charge for palladium are discussed and compared with those for platinum. (English)

In Situ Gravimetry of Corrosion of Iron Thin Films Combined with Surface Analytical Techniques

Masahiro Seo and Kengo Yoshida

Proc. 12th International Corrosion Congress,
Vol. 5B, pp. 3878-3886 (1993).

Corrosion and passivation of electroplated iron thin film in pH 6.48 boric acid-sodium borate solution were investigated by using the quartz crystal microbalance (QCM) technique combined with Auger electron spectroscopy (AES) for a better understanding of the corrosion of metal thin films. Moreover, the differences in corrosion behavior between iron thin films and bulk iron were examined.

The passivation potential of iron thin films was higher than that of bulk iron. Bulk iron was more easily passivated than iron thin films. No impurities were detected in iron thin film within the detection limit of AES. The differences in corrosion behavior between thin film and bulk, therefore, were attributed to a difference in structure.

The significant dissolution of iron preceded the formation of the passive film for passivation of iron thin films. The predominant process of passivation of iron thin films was the anodic deposition of ferrous ions once dissolved, which was supported by Auger results revealing the presence of significant amounts of boron in the passive film.

The anodic current of iron dissolution and cathodic current of hydrogen evolution could be separately obtained as a function of electrode potential from the mass change of iron thin films measured during galvanostatic polarization near the corrosion potential. (English)

Analysis of Solidification Path of Al-Ge-Si Ternary Alloy

Kenichi Ohsasa, Mitsuhiro Ohmiya, Tatsuya Ohmi
and Masayuki Kudoh

J. JILM, 43, 139-145 (1993).

The solidification paths of Al-Ge-Si ternary alloy under the conditions of the equilibrium and non-equilibrium solidification were analyzed on the basis of the thermodynamic calculation. Subregular solution model was used to describe the Gibbs free energy of the ternary solution phases such as liquid, fcc and diamond structure phases. The excess free energy of the ternary solution phases were calculated from the interaction parameters of the three binary systems which construct the ternary system. In order to confirm the validity of the calculation, thermal analysis of Al-25.5%Ge-16.0%Si ternary alloy was carried out and the Ge content of primary crystals in the solidified alloy was measured by an electron probe micro analyzer. As a result, the measured Ge content agreed well with the calculated one. and the measured temperatures at the start of solidification, the start of eutectic reaction and the end of solidification corresponded completely with the calculated non-equilibrium solidification path. (Japanese)

Analysis of Solidification Path of Aluminum Base Ternary Alloy

Kenichi Ohsasa Mitsuhiro Ohmiya, Masayuki Kudoh
and Tatsuya Ohmi

Bulletin of the Faculty of Engineering Hokkaido
University, No. 162, 163-172 (1993).

Solidification paths of Al-Ge-Si and Al-Cu-Si ternary alloys under the conditions of the equilibrium and non-equilibrium solidification were analyzed on the basis of thermodynamic calculation. Subregular solution model was used to describe the Gibbs free energy of the phases in the ternary alloys. The excess free energy of the phases were calculated from the interaction parameters of the binary systems which construct the ternary systems. The changes in fraction solid and compositions of ternary solution phases during the solidification of the ternary alloys were calculated. As a result, the experimentally obtaind temperatures such as the start of solidification, the start of eutectic and the end of solidification agreed well with the calculated non-equilibrium solidification path.
(Japanese)